

Research Paper**Carbonate rocks originated from Central Peloponnese, Greece
- Quality specifications for their use in gas desulfurisation at
Megalopolis Thermo-Electrical station****Stamatina Seferli¹, Theophilos Valsamidis^{1*}****¹Faculty of Geology and Geoenvironment, National and Kapodistrian University
of Athens, 15784, Zografou, Athens, Greece*****Corresponding author****E-mail addresses: seferlimatina@gmail.com , theovalsam@hotmail.com****Abstract**

Greece holds significant amounts of lignite deposits, whose exploitation has been a major contributor to its energy development, to date. Lignite combustion produces gas pollutants, as by-products, which are emitted from the Thermo-Electrical Stations on daily basis and especially sulfur oxides, which can contribute to air pollution, if the appropriate preventive measures are not taken. Oxides' capture is achieved using limestone, which is abundant in our country, provided that it fulfils certain standards. Therefore, it is deemed necessary to study the area surrounding the mineral deposit rocks, in order to create an excavation, the product of which is going to be used for the aforementioned purpose.

Keywords: *limestone, carbonates, Peloponnese, environmental use, gas desulfurisation, lignite*

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Περίληψη

Η Ελλάδα κατέχει σημαντικά αποθέματα λιγνιτικών αποθέσεων, των οποίων η αξιοποίηση είναι ένας κύριος παράγοντας της ενεργειακής της ανάπτυξης διαχρονικά. Η καύση του λιγνίτη παράγει αέριους ρύπους σαν παραπροϊόντα, οι οποίοι ελευθερώνονται από τους Ατμο-Ηλεκτρικούς σταθμούς καθημερινά και πιο συγκεκριμένα οξείδια του θείου, τα οποία συμβάλλουν στην αέρια ρύπανση, εάν τα απαραίτητα προστατευτικά μέτρα δεν λαμβάνονται. Η δέσμευση των οξειδίων επιτυγχάνεται με τη χρήση ασβεστολίθου, ο οποίος υπάρχει σε αφθονία στη χώρα, δεδομένου ότι πληροί συγκεκριμένες προδιαγραφές. Συνεπώς κρίνεται αναγκαία η μελέτη της περιοχής πέριξ των λιγνιτικών αποθέσεων, με σκοπό να δημιουργηθεί μια εξόρυξη, τα προϊόντα της οποίας θα χρησιμοποιηθούν στον προαναφερθέντα σκοπό.

Λέξεις κλειδιά: ασβεστόλιθος, ανθρακικά πετρώματα, Πελοπόννησος, περιβαλλοντική χρήση, αποθείωση καυσαερίου, λιγνίτης

1. Introduction

The study area is situated in the heart of the Peloponnese (Fig. 1). More specifically, it is the mountainous region of Mainalo, located SW of the prefecture's capital, Tripoli and NE of the power plant and the city of Megalopoli. It is demarcated from Psili Rachi, Palamari and Pavlia villages to the north, Palamari village to the west, Vaggos village to the south and the region of Koukouras – Kako Tsourmo to the east. It also contains villages Valtsetsi, Karatoulas and Kaloni, as well as the river Elissonas.

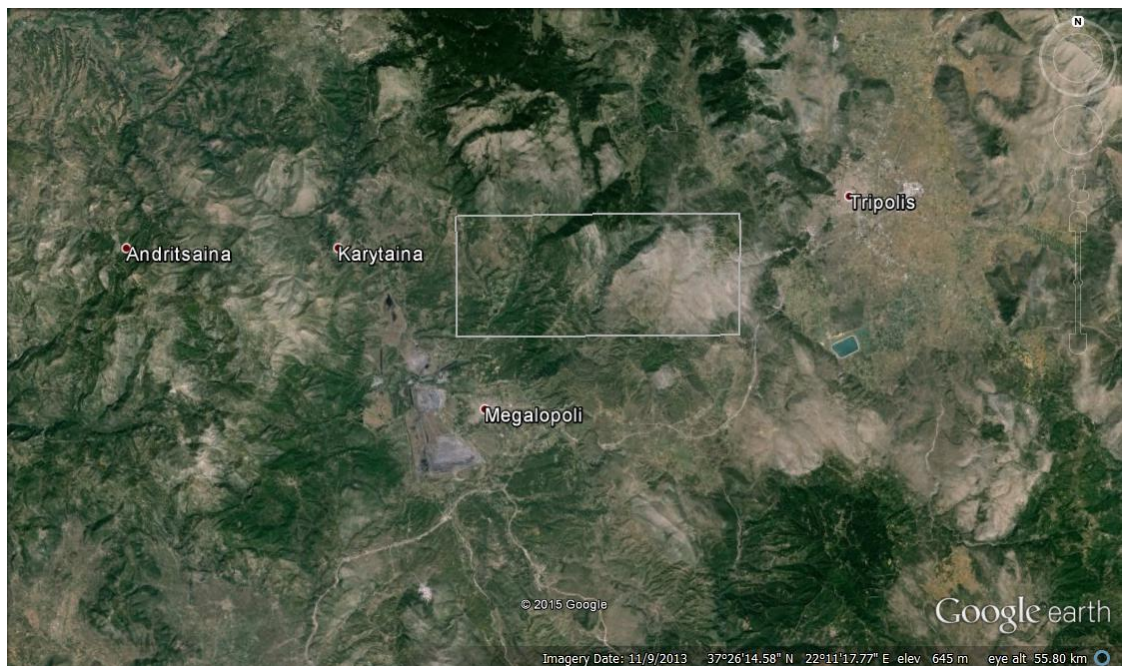


Fig. 1: Study area (white box) using a Google Earth image.

The formations are part of the External Hellenides zones, more specifically of the units of Tripolis and Pindos (Papanikolaou, 1986). They are mostly represented by carbonate formations that vary in age, deposit conditions, macro and microscopic characteristics, resulting to different rock composition, from pure grey limestone to dolomite and conclude to different uses when extracted. The different types of carbonates according to their age of deposition are the Jurassic, Cretaceous and Palaeocene – Eocene carbonates of Tripolis and Upper Cretaceous carbonates of Pindos.

Greece relies on coal to cover its internal energy needs and more specifically on lignite deposits. The resources are low in energy, especially compared to the rich coal other countries own and use, but sufficient for covering the country's energy needs for the foreseeable future. For this reason, open pit mine units that excavate, transport and burn the lignite deposits have been created, wherever that seemed profitable, like in the Florina – Ptolemaida field, or the Megalopolis field. Lignite is the most common form of coal in Greece, used for energy production. It contains humidity up to 55%, while their heating value displays a wide range of values, according to their nature and quality, varying from 900 cal/kg for the Pleistocene peat lignite of Megalopoli to 5000 cal/kg for the Cenozoic lignite of Thrace.

The Megalopoli's lignite has a light – dark brown or black colour and is rich in plant residues and fossils, especially where in contact with inorganic sediments (I.C.C.P, 1993). The main minerals contained in lignite are quartz, clay minerals, pyrite, calcite and feldspar. In terms of elemental composition, the average content of the main elements in the form of oxides in Megalopolis lignite ash is SiO₂ 29,5%, Al₂O₃ 14%, Fe₂O₃+FeO 11,8%, CaO 15,6%, MgO 2,2%, Na₂O+K₂O 1,7% and P₂O₅ 0,4% (Marinos et al., 1959). The concentrations of some trace elements in dry lignite samples are Mn 580 ppm, Zn 430 ppm, Cu 500 ppm and Pb 70 ppm (Aggelopoulos, 1985). Regarding the macerals, the vitrinite group is dominant with 71-92% w/v (Sakorafa and Michailidis, 1997), which demonstrates that Megalopolis lignite derives from plant residues, rich in cellulose, which are shattered due to biological, chemical or mechanical causes, during the carbonation, result of their low durability. As for the chemical characteristics, its average humidity is 59,3%, the average dry ash percentage is 32,6%, the average volatile components are 41,2%, the average permanent coal is 26,1%, the average heating capacity is 9,3 MJ/kg (Marinos, 1959). Finally, regarding its elemental status, it displays low levels of coal, medium levels of nitrogen and oxygen and very high levels of sulfur, downgrading its quality.

The largest active lignite quarry in Megalopoli Lignite Centre is the “Choremi” open pit mine (Fig. 2). The thickness of the lignite-hosting formation, consisting of alterations of lignite, green aluminous marls and sandy clays, is about 200 m, while the total thickness of lignite deposits is about 45 m (Sakorafa and Michailidis, 1997). The other two quarries in “Kyparissia” and “Marathousa”, though being smaller, hold significant lignite horizons, up to 25 m, as well (Athanasidou et al., 1972).

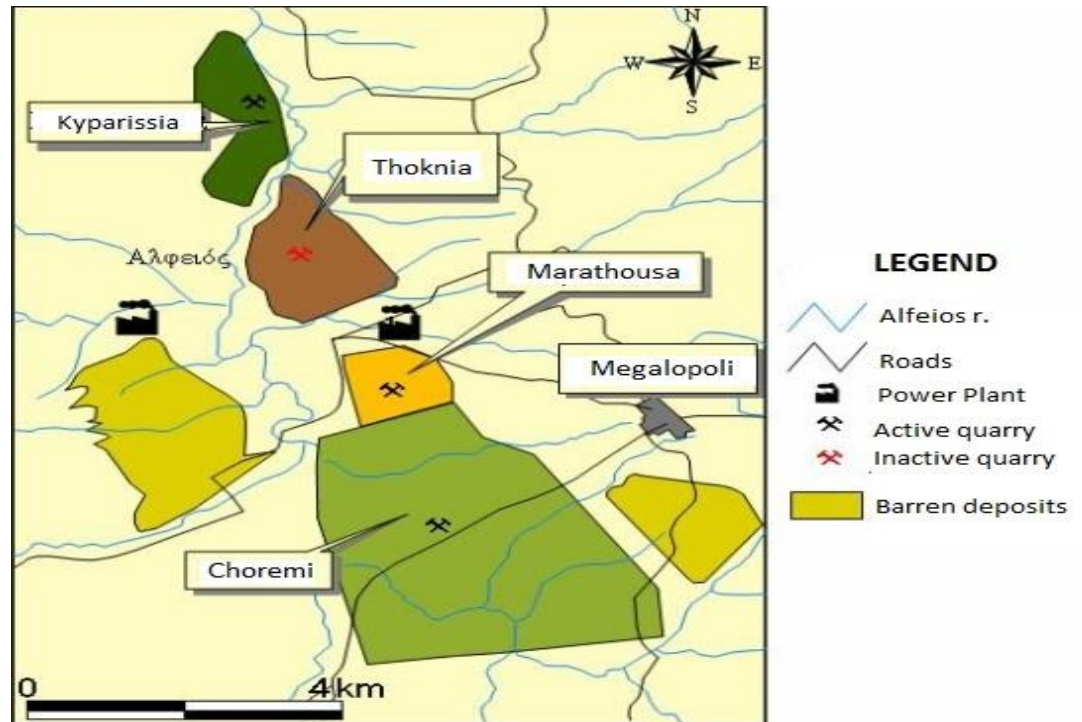


Fig. 2: Megalopolis Lignite Centre map (Source: Public Power Corporation).

Commonly, the lignite combustion releases a lot of by-products, mostly gas, to the environment. The most important of those are the sulfur oxides (SO_x), high percentage of which can lead not only to severe air, water and soil pollution of the area near the station, but also to wider environmental issues, related to air and water interaction and circulation, through the formation of acid rain due to transformation of the initial SO_x emissions into diluted H_2SO_4 in the rain water, which penetrates the soil cover of the area after having affected negatively the fauna and the local ecosystem (Chatzigiannis, 1997). The solution, the SO_x capture, can be achieved by using the most popular desulfurisation reagent, which is limestone (Johnson, 2003; Triantafyllou et al., 2004). Limestone is the most common rock in Greece, which is being excavated by a big amount of companies for various uses.

Nevertheless, the rock that contributes in desulfurisation is characterized by special attributes, regarding its mineral and chemical composition, as well as the grain size. For this reason, rocks from the wider area were examined, so as to discover if they could be used for this purpose, decreasing the transfer costs at the same time.

In Megalopolis-B (Unit IV), the Removal System Absorption of sulfur dioxide (FGD System) of Noell-KRC Company is installed. Megalopolis-B includes a boiler with lignite of low-quality fuel, intended to produce 300 MW and a maximum exhaust flow 2400.00 Nm³/h and a maximum concentration of SO₂ 14500 mg/Nm³ dry flue gas containing 6% O₂. The system of desulfurisation is a system with a limestone reactant. This means that limestone is the substance that reacts with the sulfur dioxide and the product of this reaction is slurry (emulsion), which essentially contains calcium sulfate (gypsum). The sludge is dewatered to obtain solids with concentration of 50%. The purpose of the desulfurisation system is to reduce emissions of the boiler in sulfur dioxide and mix the resulting solid residue with the other remnants of the installation (fly ash, wet ash and waste water) within a stabilisation system for a stabilized waste (Nolan, 2000). This waste is transported with conveyors in the open mine of Thoknia to be deposited (Fig. 2).

It is estimated that around 90 million € have been spent in total for the installation and operation of desulfurisation systems, while the limestone used as a reagent for the capture of SO₂ amounts to 70 tn / hour or 613200 tn / year (Public Power Corporation).

2. Materials and Methods

Carbonate samples were collected from different sites, in order to obtain a trademark type of a carbonate rock for each category that occurs in the study area. More specifically, samples of Jurassic Tripoli's dolomitic limestone in two sites near Vaggos village (VAG01, VAG02), Cretaceous Tripoli's dolomitic limestone in two sites at the Regglia region (REG01, REG02), Palaeocene – Eocene Tripoli's limestone in two sites near Valtetsi village (VAL01, VAL02) and from an active quarry in the area of Koukouras – Kako Tsourmo (LAT01, LAT02) and Upper Cretaceous Pindos' limestone in one site near Palamari village (PAL01) were collected (Fig. 3).

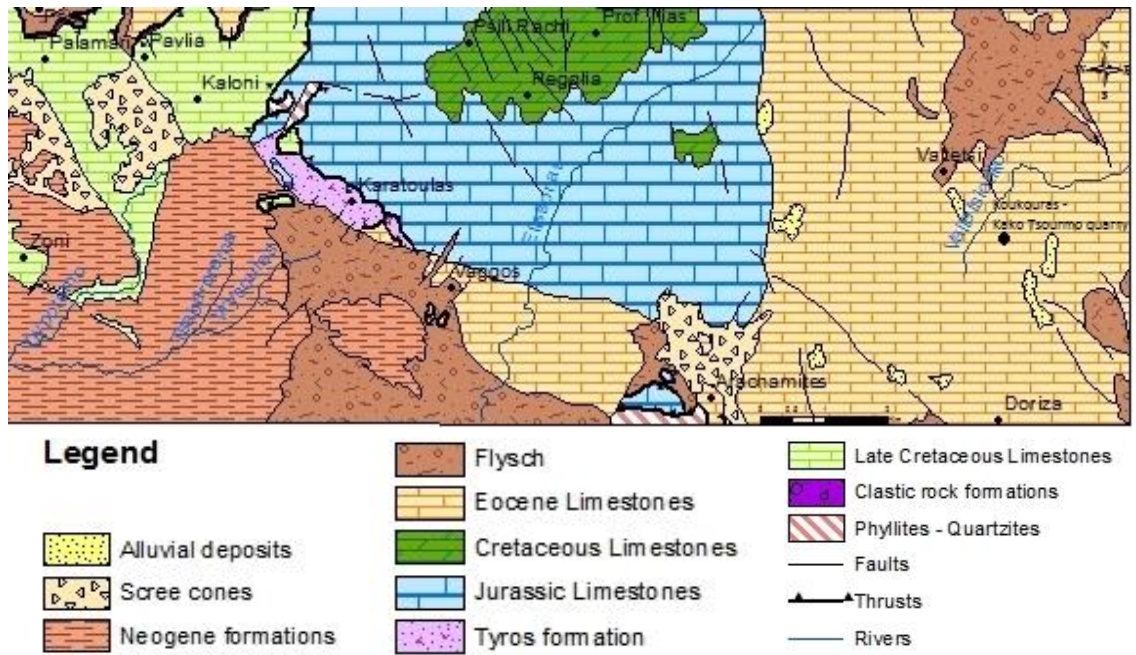


Fig. 3: Digitised area geological map.

The mineralogical determination of soil grains provides information, which in combination with the results of chemical analyses, contributes to providing a more complete picture of the distribution of the chemical elements in the study area. The soil mineralogy was studied through X-ray diffraction (XRD) on random powdered samples using a SIEMENS D-5005 diffractometer and Scanning Electron Microscope (SEM). The scanning electron microscope (SEM-EDS) was used for observations about minerals and fossils at high enlargements, as well as qualitative and quantitative chemical composition of samples. This task was carried out using flat, well-polished, thin sections, paying attention to the procedure, as the minerals could not withstand extreme polishing.

3. Results

3.1 Chemical analysis

Chemical analyses were performed in order to identify the key elements of the carbonate samples. The XRF techniques that were used to reveal the chemical compositions were performed with the aid of the TITAN Group. The elements that were crucial and required measurement were Ca, Mg, Si, Al, Fe⁺³, Mn and Zn oxides, as well as the loss on ignition (Table 1).

%	VAL01	VAL02	VAG01	VAG02
<i>SiO₂</i>	0,10	0,26	0,22	0,68
<i>Al₂O₃</i>	0,05	0,05	0,11	0,24
<i>Fe₂O₃</i>	0,00	0,01	0,08	0,14
<i>CaO</i>	55,63	56,76	55,58	54,87
<i>MgO</i>	0,63	0,62	0,37	0,47
<i>MnO (ppm)</i>	30	60	50	118
<i>ZnO (ppm)</i>	20	10	0	38
<i>LOI</i>	44,04	40,09	44,00	43,31

%	REG01	REG02	PAL01	LAT01	LAT02
<i>SiO₂</i>	0,53	0,92	29,38	0,47	3,58
<i>Al₂O₃</i>	0,23	0,07	1,17	0,20	1,11
<i>Fe₂O₃</i>	0,07	0,01	0,30	0,07	0,49
<i>CaO</i>	32,75	34,72	38,62	36,18	37,42
<i>MgO</i>	19,80	17,81	0,13	16,05	12,93
<i>MnO (ppm)</i>	394	0	2020	400	640
<i>ZnO (ppm)</i>	171	291	238	89	252
<i>LOI</i>	46,97	46,64	29,74	46,58	44,11

Table 1: Chemical analyses of the carbonate samples.

The main remarks after the analyses were the high Ca concentrations, along with the low Mg values, in VAL and VAG samples.

On the other hand, relatively high concentrations of Mg and lower of Ca were spotted in REG and LAT samples.

The main characteristic of the PAL sample was the very high values in Mn oxides and silica.

3.2 Mineralogical analysis

The XRD analysis revealed that the dominant mineral phases found in the carbonates collected were calcite, dolomite and quartz, minerals that were anticipated in those types of rocks. The most noteworthy samples were pure limestone, composed of solely calcite (Fig. 4). Such observations were made in Jurassic and Palaeocene – Eocene Tripoli's limestones.

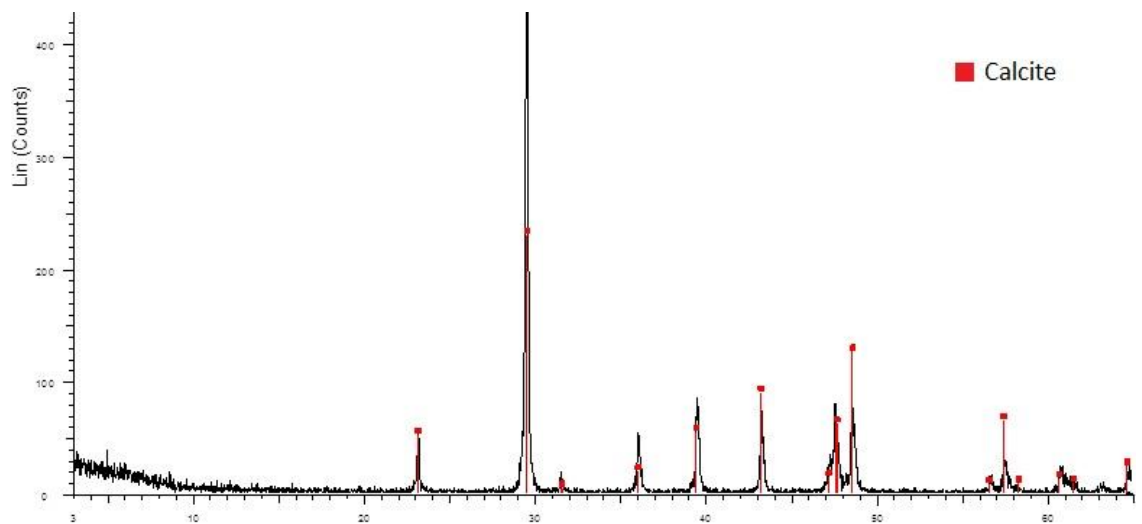


Fig. 4: Mineral Matching of Palaeocene – Eocene Tripoli's limestone.

3.3 Microanalysis

The microanalysis using the scanning electron microscope (SEM-EDS) was crucial to the competition of the project, due to the fact that it provided the opportunity to observe in very great detail each sample's mineralogy with images in very high analysis and each point's chemical interpretation, indicating all the minerals included in higher or lower percentages.

The main remarks derived from this procedure were the identification of pure calcite samples, the dolomitisation process in various levels in most samples, the conspicuous presence of quartz in some of them and the intrusions of other minerals such as chlorite or apatite that require further investigation (Fig. 5).

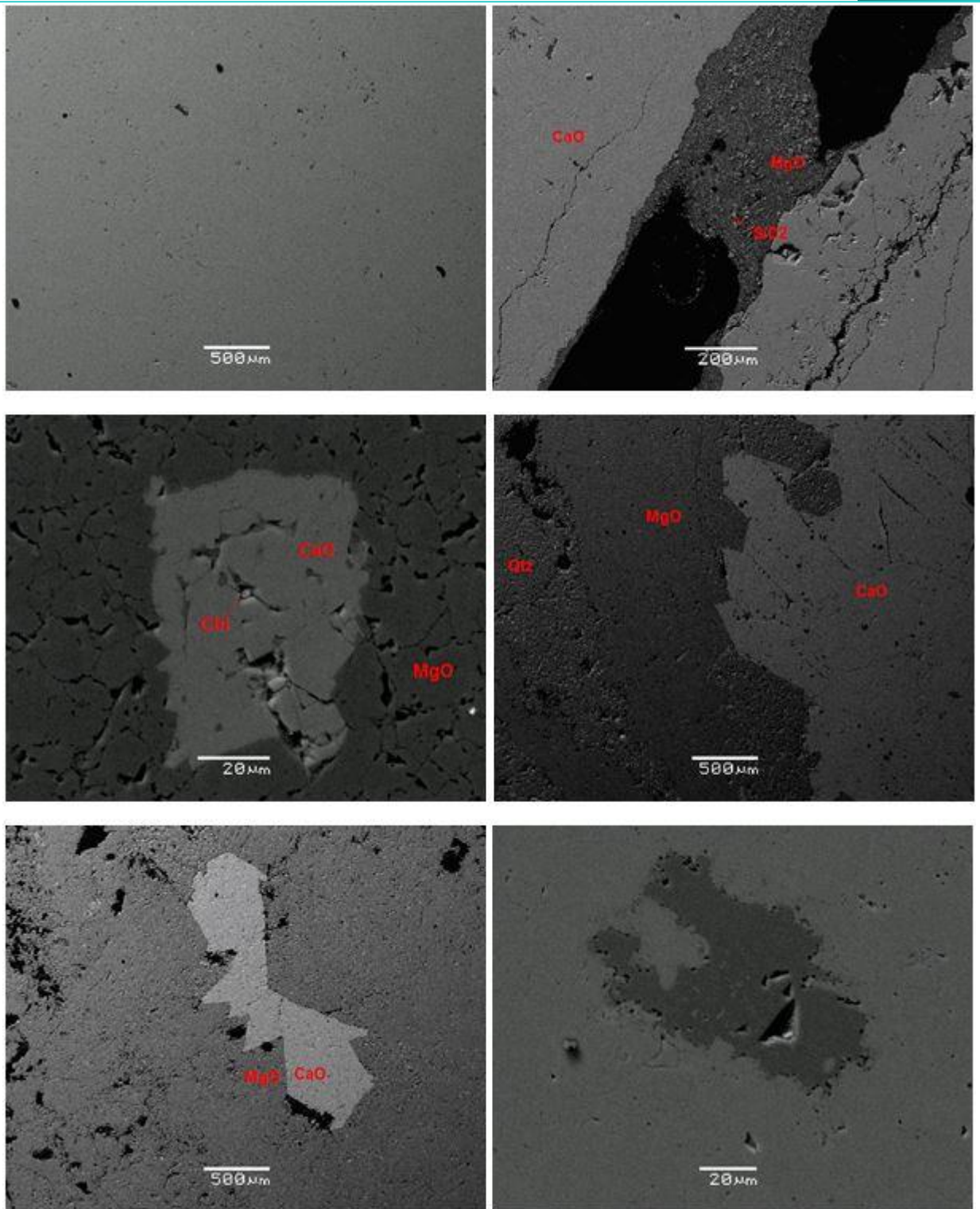


Fig. 5: SEM images: top row) Pure Calcite - dolomitization in progress, middle row) Calcite in a matrix of Dolomite. Inclusions of chlorite are observed in the first, - comparison of Calcite – Dolomite – Quartz, bottom row) Dolomite and Calcite in the final stage of dolomitization - dolomitization in progress

4. Discussion

The carbonates that were analysed should be compared with the standard values and the permissible limits set by the Public Power Corporation (PPC) (Table 2), regarding their use in units III and IV of Megalopoli's Thermoelectrical Station, in order to be considered appropriate or not for gas desulfurisation.

Technical Characteristics	Unit III	Unit IV
(CaO)	51-56% w/w	52-56% w/w
Humidity	<2,5%	<2,5%
(MgO)	<5%	<5%
(CO ₂)	<44%	<40-44%
Grain size	<14mm	<16mm
(SiO ₂)	<1,8%	<1,16%
(Fe ₂ O ₃)	<0,58%	<0,5%
(Al ₂ O ₃)		<0,25%
(Mn)	<100 mg/kg	<100 mg/kg
(Zn)	<30 mg/kg	<30 mg/kg
Band Work Index	<15 kWh/t	<15 kWh/t

Table 2: Permissible limits for use in Units III and IV of Megalopolis Power Station (Public Power Corporation).

After analysing the samples with the different methods and taking the PPC limits (Table 2) into consideration, the following were concluded:

- The samples VAL 01, VAL 02, VAG 01 and VAG 02 are chosen, since they match the standards of the technical characteristics, where very low percentage of MgO and SiO₂ were distinguished in chemical analyses. Moreover, dolomite and quartz are absent on XRD diagrams, while only a small percentage of dolomitic material exists in microanalysis.
- The sample REG 01 is rejected due to the high percentage of MgO, Mn and Zn oxides, in contrast with the low percentage of CaO that the chemical analysis indicated. Still, the loss on ignition is higher than the permissible limit. The mineralogical analysis showed that the sample contains calcite, dolomite and quartz while microanalysis showed that dolomitic material constitutes the majority of the sample, although dedolomitisation is at a later state.
- The sample REG 02 is rejected due to the high percentage of MgO, and Zn oxides, in contrast with the low percentage of CaO that the chemical analysis indicated. Still, the loss on ignition is higher than the permissible limit. The mineralogical analysis showed that the sample contains calcite and dolomite, while microanalysis showed that

dolomitic material constitutes the majority of the sample, although dedolomitisation is at a later state.

- The sample PAL 01 is rejected due to the high percentage of SiO₂, Al₂O₃, Mn and Zn oxides, in contrast with the low percentage of CaO that the chemical analysis indicated. Still, the loss on ignition is higher than the permissible limit. The mineralogical analysis showed that the sample contains calcite and quartz, while the microanalysis didn't indicate quartz as expected.
- The sample LAT 01 is rejected due to the high percentage of MgO, Mn and Zn oxides, in contrast with the low percentage of CaO that the chemical analysis indicated. Still, the loss on ignition is higher than the permissible limit. The mineralogical analysis showed that the sample contains calcite and dolomite, while microanalysis showed high percentage of Mg.
- The sample LAT 02 is rejected due to the high percentage of SiO₂, Al₂O₃, Mn and Zn oxides, in contrast with the low percentage of CaO that the chemical analysis indicated. Still, the calcination loss is higher than the permissible limit. The mineralogical analysis showed that the sample contains calcite, dolomite and quartz, while microanalysis showed high percentage of Mg.

Apart from the quality specifications, in order to activate a new quarrying site, law 2115/93, Article 3 (GG 15A/15-2-1993) of the mining code should be obeyed. This law states that: "*Inside an excavation area and 1 km away from it, the expansion of urban plan or the creation of an independent town planning or the construction of any building, except from those serving the quarrying activity, is forbidden*". According to this law, the nearest town, which in this case is Valtetsi and Vaggos villages, should be in a distance greater than 1 km away from the quarrying area. This criterion is fulfilled as the sampling areas are 2-3 km at least away from them. Moreover, there is absence of other areas, like archaeological sites or Natura zones that would forbid the quarrying procedure.

Knowing from neighboring quarries that the limestone extraction cost is around 3-3,5 €/ton and that the daily output reaches 3000 tones, we consider that a medium size exploitation (~200 acres), may prove quite profitable. The area is accessible by existing roads and should the mountain be considered "friendly" to a surface excavation, namely if the inclinations are favorable to surface mining without critical exposure to nearby villages, the activity could be considered possible.

As far as the rest of the area's rocks are concerned, there are a lot of different uses that Central Peloponnese carbonate rocks may be suitable for. Indicatively, limestone is one

of the most common and basic fluxes in metallurgy. Most of the copper and molybdenum ores are acidic, and a basic flux such as limestone must be used to process them. It is involved in approximately 75% in the composition of the raw material in cement production, while up to 35% in the final product – cement (Imbabi M. S., 2012). More specifically, it provides the CaO, which is combined with elements as Al, Fe, Si thus creating complex compounds of clinker cement, a connecting material of fine powder with hydraulic properties, which when mixed with water, forms a paste that thickens and hardens through hydration reactions and mechanisms; after hardening, it retains strength and stability even under water (Boynton S.R., 1980, Oates J. A. H., 1998). Moreover, it finds use as an agricultural fertilizer, since the calcium in soil is important not only as a plant nutrient, but also because it has the ability to retain the desired biological and physical condition of the soil. We use very finely grained CaCO_3 as fertilizer to increase the pH of acidic soils that do not allow maximum plant growth. Also, it finds use as a raw material in ceramic materials, mainly as an adhesive and as a refractory when it has low silicon concentration.

Limestone can be used as filler in various pharmaceutical applications such as in the manufacturing of food supplements and other calcium - rich preparations for treatment of diseases such as osteoporosis. The detailed precipitated calcium carbonate (PCC 0,5-3 μm) is extremely popular in pharmaceutical applications due to the very low levels of trace metals it contains. Animals' bones consist almost exclusively of Ca and P. Pure limestone, mixed with potassium phosphate and ground bones, is added to pet food. This kind of diet contributes to a healthy physique and skeletal tissues of animals and faster development. Besides that, carbonates with Ca percentage not exceeding 10% can be used as raw material in the manufacturing of glass objects, namely in the glass industry.

In addition, both limestone and other carbonate rocks are used as fillers in fertilizers, paints, plastics, insecticides and asphalts. Its use as filler is due to high solubility in acids, the small grains of hardness, the low cost and abundance in natural nature. Furthermore, comminuted limestone can be used to improve the physical properties of the pulp of a borehole. Finally, it finds many uses as an inert material, as a structural component, e.g. in the manufacture of concrete, copper filter to protect boreholes, jetties and breakwaters and as a substrate in asphalting.

5. Conclusions

In conclusion, samples VAL 01, VAL 02, VAG 01 and VAG 02 are technically suitable for desulfurisation, since they present low dolomitic and siliceous material. For the reasons mentioned above, as well as for reducing the time and cost of transferring, we encourage the limestone's mining from the area of Valtetsi and Vaggos.

As far as the rejected carbonate samples are concerned, taking their physical and chemical characteristics into consideration, we concluded about the use that each type can accomplish. In particular, the Jurassic and the Eocene limestones of Tripolis apart from the desulfurisation, can be used as building stones, inert materials, lime production, soil additives, processing sugar beet and in glass pane industry, but could not be used as white fillers due to their greyish colour. The Cretaceous limestones of Tripolis can be used as building stones, inert materials and fertilizer. The Upper Cretaceous limestones of Pindos can be used as building stones, inert materials and soil additives. Finally, none of the above types could be used for cement production, animal food or in the tire industry.

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